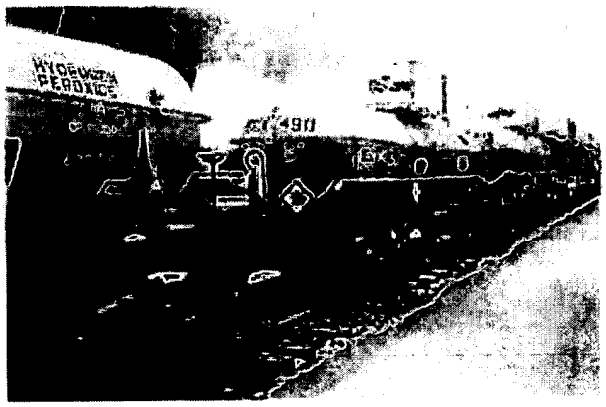
INTRODUCTION TO HYDROGEN PEROXIDE

physical and chemical properties of hydrogen peroxide

Contents:



Exh. 5. + A

Electrical Properties

1. Conductivity
2. Dielectric constant
3. Magnetic susceptibility

Radiation Properties

1. Refractive index
2. Magneto-optic rotation
3. Microwave absorption spectrum
4. Infrared absorption spectrum
5. Raman spectrum
6. Visible spectrum
7. Ultraviolet absorption spectrum

Solubility Properties

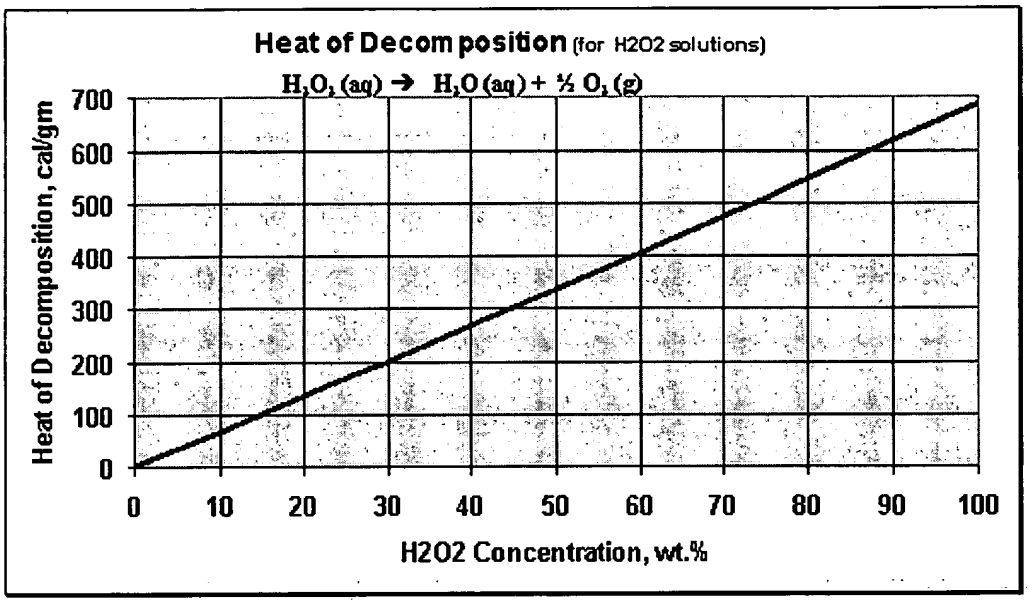
Solubility / Distribution coefficients in selected solvents

1. Alkanes
2. Aromatics
3. Ethers
4. Alcohols
5. Other

[To Frequently Asked Questions (FAQ)]

Home Email Us! Join Our Mailing List! Search What's New Links

5. Heat of decomposition



P.A. Giguere, *Complements au Nouveau Traite de Chemie Minerale – No. 4 Peroxyde d'Hydrogene et Polyoxydes d'Hydrogene*, Paris, Mason, p.181 (1975)

NOTES: 1. The standard free energy change (ΔF^o) is -27.92 kcal/mole at 25 °C

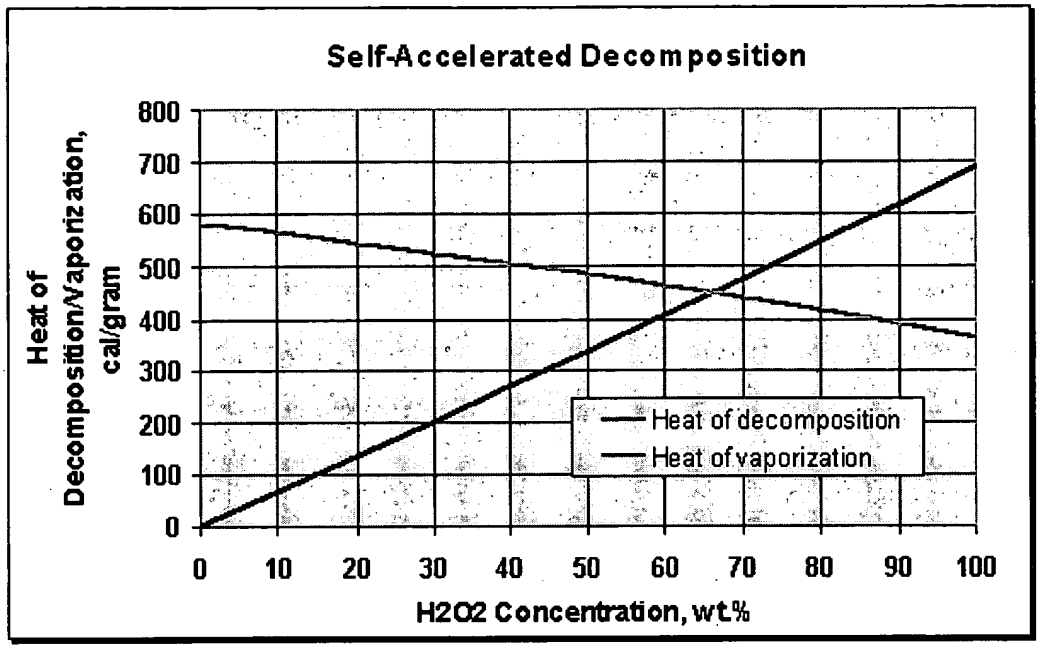
2. Rapid decomposition of concentrated H_2O_2 solutions may not be complete, with concentrations up to 10% remaining.

6. Heat, Free Energy, and Equilibrium Constant

$$H_2O_2\ (g) \rightarrow H_2O\ (g) + \tfrac{1}{2}\ O_2\ (g) \qquad \Delta H_{dec} = 23.44 \text{ kcal/mole}$$

W.C. Schumb, C.N. Satterfield, R.L. Wentworth. *Hydrogen Peroxide*, ACS Monograph, Reinhold Publishing, pg. 251 (1955).

7. Decomposition products



NOTES:
1. H_2O_2 decomposition is highly exothermic (23.44 kcal/mole). Even 10% H_2O_2 can boil if it becomes grossly contaminated.
2. The effect of temperature is such that an increase of 10 °C increases the rate of decomposition by a factor of 2.3 (i.e., a first order rate equation). Therefore, decomposition can accelerate if the solution becomes grossly contaminated.
3. As the concentration of H_2O_2 in solution increases, there is less water to absorb the heat of decomposition. A crossover occurs at 63-64% H_2O_2 where rapid, accelerated decomposition becomes self-sustaining and the concentration of H_2O_2 in the decomposing solution can actually increase.

---

10. Free energy of formation

H_2 (g) + O_2 (g) → H_2O_2 (aq) $\quad \Delta F^o$ = -31.95 kcal/mole (25 °C)

Temp., °K	ΔH, kcal/mole	ΔF, kcal/mole	log K
0	-31.26	-31.26	---
298	-32.52	-25.24	18.51
300	-32.54	-25.20	18.35
400	-32.80	-22.71	12.41
500	-33.01	-20.16	8.81
600	-33.15	-17.58	6.40
700	-33.30	-14.98	4.68
800	-33.38	-12.36	3.38
900	-33.48	-9.73	2.36
1000	-33.56	-7.08	1.55
1100	-33.63	-4.43	0.88
1200	-33.69	-1.83	0.33
1300	-33.73	0.92	-0.15
1400	-33.77	3.56	-0.56
1500	-33.79	6.24	-0.91

11. Standard electrode potentials

H_2O_2 contains oxygen in a state of oxidation midway between molecular oxygen and water.

	Reduction →		
Oxygen moiety	O_2	⇔ H_2O_2 ⇔	H_2O
Oxygen valence	0	-1	-2
	← Oxidation		

$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$ $E^o = -0.682$ V

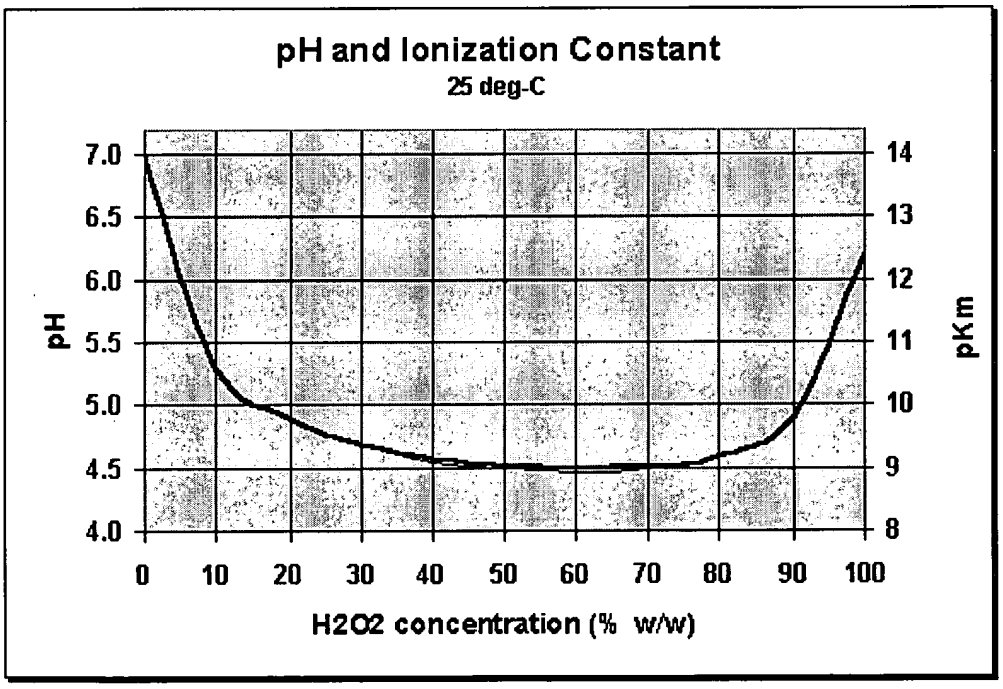
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ $E^o = 1.776$ V

For perhydroxyl ion (HO_2^-):

$OH^- + HO_2^- \rightarrow O_2 + H_2O + 2e^-$ $E_B^o = 0.084$ V

$3OH^- \rightarrow HO_2^- + H_2O + 2e^-$ $E_B^o = -0.87$ V

12. pH and Ionization Constant



13. Dissociation: Heat, Free Energy, and Equilibrium Constant

	ΔH^o	ΔF^o (kcal/mole)
Nonionic		
H_2O_2 (g) = H_2O (g) + O(g)	+ 33.90	+ 25.60
	+ 136.72	+ 122.41